ARPA ORDER NO.: 189-1
6L10 Technology Assessments

R-1579-ARPA
January 1976

Advanced Concepts of Superconductivity: A Comparative Review of Soviet and American Research. Part II. High-Pressure Superconductivity

Y. Ksander and S. Singer

A Report prepared for

DEFENSE ADVANCED RESEARCH PROJECTS AGENCY

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PREFACE

This Report is part of a continuing Rand study, sponsored by the Defense Advanced Research Projects Agency, of significant aspects of Soviet scientific research. It is the second in a series that considers superconductivity, an area in which the Soviet Union maintains a strong and active technological posture. The present Report treats high-pressure superconductivity (HPS); an earlier Report by the same authors -- *Advanced Concepts of Superconductivity: A Comparative Review of Soviet and American Research. Part I. High-Temperature Superconductivity*, R-1401-ARPA, January 1974 -- dealt with high-temperature superconductivity (HTS); a subsequent report will discuss high-critical-field superconductivity (HFS) and related subjects.

The Report is based on a comprehensive -- although not exhaustive -- coverage of U.S. and Soviet open-source literature, most of which appeared between 1971 and mid-1974, a period of intensive Soviet publishing activity in the area of HPS. It is designed to present the fundamental concepts of HPS, the significance of experimental results, and an evaluation of research in each country.

As was the case in the earlier Report in this series, we have chosen to devote more attention to the Soviet research than to the American in the belief that it is of greater interest here. The Soviet Union continues to be more aware of the work done in the United States than vice versa.

The Soviet Union is a leader in high-pressure physics research in general and HPS in particular. The incentive of new materials -- such as industrial synthetic diamonds -- spurred construction of large static presses. The Soviet capability in this area exceeds that of any other country. In terms of advancement of research in HPS, this is a significant advantage.

We believe the publication of this Report is warranted and timely for the following reasons:

- There is great scientific interest in the properties of materials under ultrahigh pressures.
- Formation of modifications under high pressures has been demonstrated; modifications, as new substances, may have novel properties, including higher superconducting temperature.
- High-pressure capability on the order of millions of atmospheres is at hand.
- Soviet support of experimental research in high-pressure superconductivity is greater than American and has placed the USSR in a position of major strength in this field.

SUMMARY

This Report is the second in a series comparing Soviet and American research in advanced concepts of superconductivity. It focuses on the effects of high pressure on the superconducting properties of materials. Pressure is a significant variable, both in revealing important features of superconductivity and how it occurs in materials and, potentially, in producing substances of increased value as superconductors.

Section I summarizes the qualitative effects of pressure on material properties. The formation of new phases and new structures by the application of pressure to substances that are normal (i.e., nonsuperconducting) at atmospheric pressure is discussed. Some of these are metastable and continue to exist under certain conditions after the pressure is removed.

Section II describes the methods of obtaining high pressures, with emphasis on Bridgman-type mechanical presses capable of static pressures on the order of several megabars. The experimental results of significant recent research with pressure-induced superconductors in the last few years (1971-1974) are summarized in Section III, which emphasizes Soviet work.

The findings of the first three sections are synthesized in Section IV to provide assessment of the American and Soviet efforts in HPS. Research institutions and the affiliated personnel in each country are identified and listed in Tables 3 and 4. The largest and most important Soviet organization in this field -- the Institute of High Pressure Physics -- is featured in the context of present and future developments.

The major findings of this Report are:

1. The transformation of materials by the application of pressure is not fully understood, and techniques for obtaining high pressures in laboratory studies are difficult.

2. Significant achievements have been made in attaining high static pressures by improving classical pressure devices.
3. The capability to apply pressure on the order of millions of atmospheres is now at hand.
4. Development of very hard structural materials has been significant in attaining superhigh pressures.
5. Compression can bring about superconductivity at greater temperatures through the formation of modifications that, as new substances, possess high T_c, or superconducting transition temperature.
6. Experimental data on the effects of pressure on superconductivity are extensive, although the pressure range is limited; measurements of the desired volume parameters are almost completely lacking.
7. The USSR now has the largest and most active groups with research equipment adequate to place it in a leading position.
8. The principal thrust of the Soviet high-pressure research is:
   - o development of new materials
   - o search for new superconductors.
9. The transformation of hydrogen to a metal under superhigh pressure has become one of the major research interests of the Soviet new materials program.
10. The volume and purpose of high-pressure physics research in the United States has fluctuated since the death of P. W. Bridgman and is now relatively modest. In contrast, Soviet research has expanded rapidly in recent years. However, up to now, far more new substances have been produced in U.S. research.
11. Industrial laboratories in the United States have high-pressure capability, but work on superconductivity is not given major attention. Superconductivity measurements are often auxiliary to the study of other parameters. U.S. scientists are generally well informed, and basic problems are well understood.

12. The Soviets have a larger experimental capability. Several years would be needed to bring the U.S. capability to parity following the decision to make such an effort.
13. Contrasts in the Soviet and American programs have roots in underlying research goals: Contrary to the usual positions, in this field the Soviets are relatively materials oriented, while Americans show greatest interest in the basic physical aspects.
14. The discovery of superconductors with greatly increased operating temperatures (described in our previous Report) is a major Soviet goal, and the high-pressure work provides an additional avenue toward achieving this goal. Materials derived from research in this field could have enormous impact on both civilian and military technologies.

ACKNOWLEDGMENTS

The authors wish to thank Professor William A. Little of Stanford University, Professor Bernd T. Matthias of the University of California at San Diego and Bell Telephone Laboratories, and Dr. James E. Schirber of Sandia Laboratories for their useful comments and suggestions, but take full responsibility for the views expressed in the Report. They also wish to acknowledge the effort of Stuart G. Hibben and John Kourilo of Informatics, Inc., who aided in the search of the Soviet open-source literature.

CONTENTS

I. EFFECTS OF HIGH PRESSURE ON MATERIALS

Pressure is a significant parameter in superconductivity: One-third of the known superconducting elements exhibit this property only in forms produced under pressure. The earliest study of the effect of pressure on superconductivity was made in 1925 by Kamerlingh Onnes, the discoverer of superconductivity. The experimental pressures accessible to him, limited to less than 150 atmospheres, were insufficient to produce appreciable effects. The development of experimental equipment for high-pressure studies proved difficult, and historically, slow progress was made in the few laboratories where interest in the area existed. The capability of applying pressures of the order of millions of atmospheres is now at hand, and there is great scientific interest in material properties requiring study at pressures of this magnitude, which has been awaiting the availability of such apparatus.

A. VARIATION OF PROPERTIES WITH PRESSURE

The application of pressure to materials provides a method by which the properties can be altered. This effect is comparable to changing the chemical composition or temperature of materials. In some cases, the alteration by pressure is so drastic that an essentially new substance is formed. In the case of solids, a considerable pressure -- several thousandfold greater than atmospheric -- may be required before a change can be detected in even the most sensitive physical properties.

The effects of pressure applied to a liquid or solid may be described somewhat arbitrarily by the results observed with progressively increasing compression. At first, the outer electrons of the individual atoms and molecules feel the pinch. Interactions among the molecules are affected, and in a liquid, for example, the viscosity changes. The electrons between atoms are then affected, resulting in changes in orbital or bonding energies, which are reflected in the electronic spectra [10, 14, 32].

The change in electron density near the atomic nucleus on compression can affect radioactive decay involving electron capture. A change in rate of 0.002 percent per kilobar was observed for the conversion of beryllium-7 to lithium-7 [21].

B. FORMATION OF NEW PHASES AND NEW MATERIALS

The changes in interatomic electron interaction, or bonding, with pressure are, of course, equivalent to the production of a material with different properties [14]. These are often accompanied by a change in crystal structure or the formation of a new chemical substance. Under pressure, a new bonding orbital may be given greater stability, and more compact packing may be achieved by rearrangement of nuclei in a crystal, leading to the alteration in crystalline or molecular structure [40].

With increasing pressure, all substances approach in structure an identical, best-packed structural lattice [1]. Chemical bonds are eventually destroyed, producing ionic crystals with high free-electron density and the associated metal conductivity [17, 18, 38]. The vibrational energy and frequency of the heavy nuclei of the crystal lattice, reflected in the Debye temperature, increase generally with the pressure. At sufficiently high pressures, the lower region of which is now just accessible to the most advanced experimental methods, the elements are increasingly stripped of extranuclear electrons, and great densities characteristic of astronomical bodies occur.

C. THEORETICAL STUDIES OF PRESSURE EFFECTS

In a study of the basic properties of matter under pressure, specifically, electron and ion interactions, Abrikosov [1] was unable to determine whether superconductivity will invariably occur in the general case. The formation of electron bound pairs depends on short wavelength phonons, and a complete determination of the phonon spectrum is required to answer the question. The binding energy of electron pairs was obtained as an exponential expression, however, with pressure as a negative exponent. This indicates that the superconductivity under pressure is an exponentially small effect and that the gap -- the electron binding

in the Bardeen-Cooper-Schrieffer (BCS) theory -- decreases with compression. This is equivalent to a reduction of T_c, the superconducting transition temperature, with increase in pressure.

The BCS theory provides the generally used basis for analyzing the effects of pressure on superconductivity. Its simple form*

$$T_c = 0.85\theta_D \exp[-1/N(0)V]$$

indicates three parameters through which pressure may affect the temperature of transition to the superconducting state, namely, the Debye temperature θ_D, the density of states N(0), and the electron interaction V.

The Debye temperature, which is also related to the vibrational frequency of ions in a crystal lattice, increases with compression. The change is in accordance with the increase of electric conductivity of normal metals with pressure [11]. But there is no correlation with the critical temperature T_c, which, for many metals, in fact decreases on compression, often even more rapidly than the Debye temperature increases.

The density of states and the electron interaction remain as possible sources of the change in T_c with pressure. The density of states can be evaluated independently through the electronic specific heat. The changes in the density of states and in the Debye temperature are sufficient to account for the decrease in T_c with pressure for zinc, cadmium, and Zr-Nb-Mo alloys [10, 11]. This implies that the electron-phonon interaction remains constant with pressure change in these metals. In other work, the density of states has been considered constant in certain metals, making it necessary to account for change in T_c by variation in the electron interaction with pressure. In some cases it appears that both the density of states and the interaction parameter vary with pressure.

*The equation is frequently given as $T_c = 1.14 \frac{\hbar\omega}{k} \exp[-1/N(0)V]$.

The general effect of increasing pressure on the decrease of T_c from an approximation with the free electron model for increasing densities [17] is shown as:

Density (g/cm^3)		T_c (K)
1	....	200
10	....	10
100	....	10^{-6}
1000	....	10^{-8}

Soviet researchers consider the destruction of superconductivity by very high pressure a major theoretical question and a significant experimental goal. The general behavior of superconductors as T_c decreases with increasing pressure may be rationalized qualitatively. As T_c approaches zero, the product of the density of states and the interaction parameter in the BCS theory must also approach zero. The density of states, however, cannot become zero, since a metallic state remains. It is the interaction parameter V, therefore, which becomes zero at the disappearance of superconductivity, when the electron-phonon interaction is insufficient to overcome the Coulomb repulsion. The critical pressure for the disappearance of superconductivity has been considered most thoroughly for cadmium, zinc, and aluminum, extrapolation providing estimates of 120, 160, and 200 kilobars, respectively [11].

D. SUMMARY OF OBSERVED PRESSURE EFFECTS ON SUPERCONDUCTIVITY

The experimental data on the effects of pressure are extensive, although the range in pressure covered for all but a few materials is limited and desired volume parameters are almost completely lacking. A brief summary is presented below to provide a general outline of what is known. Recent measurements are discussed specificallv in Section III.

Silicon, germanium, bismuth, antimony, phosphorus, tellurium, selenium, arsenic, barium, and cerium are examples of elements that are superconducting only in forms produced under pressure. Metals

not in the transition group give a regular decrease in T_c as pressure increases, provided new forms or crystallographic structures do not appear. Thallium is an exception in which the change of T_c with pressure is positive in accordance with the change in Debye temperature, but this mode is in effect only up to a few kilobars and is then replaced by a decrease at higher pressures as with other nontransition metals [11, 32, 34].

Cesium is the only alkali metal element (Group I of the periodic table) in which superconductivity has thus far been observed [51]. Cesium (V) exhibits a T_c of 1.5 K at approximately 125 kbar.

Compression can bring about superconductivity at greater temperatures through the formation of modifications -- or new substances -- possessing higher T_c. The largest number of such modifications is found in the elements of Group V of the periodic table, including bismuth, antimony, and phosphorous. Bismuth is particularly interesting in exhibiting five modifications, of which three are superconductors. It should be noted that progressive increase of pressure above that required to produce the new form normally gives the usual decrease in T_c.

In the transition metals, on the other hand, there is no general rule for the effect of pressure. T_c may increase or decrease, and the magnitude of the effect is variable. The distinction between transition and nontransition metals may be accounted for on the basis of the constrasting electronic structures. The latter possess filled electron shells, and pressure should thus always lower T_c. In the transition metals, on the other hand, there are unfilled inner shells. The Fermi surfaces are more complex, and the effect of compression on the density of states, for example, may also be complex [35].

Soviet research goals in this field were aptly summarized by the leading investigators, Brandt and Ginzburg of Moscow State University [10]:

> The search for new superconducting modifications has developed in two directions: superconductivity in forms produced by high pressure in elements and compounds that are normally not superconductors, and new forms of known superconductors. Significant successes have been achieved in both directions.

II. METHODS OF OBTAINING HIGH PRESSURE

The effects of pressure on materials are not well understood, and techniques for obtaining high pressures in the laboratory are very difficult. The obstacles are compounded when low temperatures such as those required in superconductivity must be provided in the high-pressure zone. These difficulties combined to slow progress in the study of superconductivity at high pressure. Over a quarter of a century elapsed between the early efforts of Kamerlingh Onnes, Sizoo, and de Haas at the University of Leiden and the achievement of kilobar pressures at the desired temperatures, and another two decades have gone by until the present time, when megabar pressures are at hand. The temperatures of interest in superconductivity have not yet been obtained at the highest pressures, but it appears this capability will not be long delayed, according to Soviet experimental plans. Extension of the range of pressure accessible to study is important, because the effects are in general small. Progress has tended to take the form of somewhat detailed improvements to increase the effectiveness of existing experimental apparatus and methods. Entirely new general concepts that might lead to completely different types of equipment are rare. Nevertheless, significant achievements have been made in attaining high pressure by improving classical pressure devices.

The development of high-pressure equipment has been reviewed thoroughly elsewhere (see, for example, [10, 31]). The predominant American figure in the field was P. W. Bridgman of Harvard, whose work spanned four decades and is still the basis for the most advanced apparatus of the present day. His research made the United States the leader in the area of high-pressure physics. Subsequently, a significant, still active group that developed at the University of Illinois beginning in 1950, as well as the Bell Laboratories, have continued efforts in the field. At the same time, research in Germany and the Soviet Union expanded, with both countries making significant

contributions. The Soviet Union now has the largest and most active research groups, along with adequate equipment to place it in a leading position.

A. STATIC PRESSES

The apparatus used to study the effects of pressure on superconductivity is exclusively the mechanical press, which generates and then maintains the applied pressure on a small experimental sample. Alternative methods have been developed relatively recently for producing great transient pressures for very short time periods, such as shock and detonation waves, including those provided by nuclear explosions. With the exception of the investigation of hydrogen, however, the transient pressure methods have not been utilized in problems related to superconductivity.

Two methods may be used to obtain the high-pressure region at the low temperatures of interest for the study of superconductivity. In one, the experimental sample and the pressure vessel are cooled to the desired temperature, and then the pressure is applied. Marked anisotropy can occur in this procedure through the slowing of phase transitions and the deformation of the sample because of its low plasticity and accompanying resistance to compression. In the other method, the pressure is applied first, and then the sample (or in some cases the whole pressure vessel) is cooled to the temperature at which the investigation is to be made. In this process thermal gradients may cause anisotropy in the sample if equilibrium is not attained, and the pressure can change through contraction of the pressure vessel on cooling. In general, the latter approach is more often preferred.

Bridgman designed a press in which the sample under study, contained in a cylindrical yoke, was compressed by opposed pistons, one above and one below, operating simultaneously (Figure). The appearance of alloys of increasing strength aided in increasing experimental pressures attained. Bridgman also contributed a nonleaking pressure seal that provided a positive closure by controlling the relative surface areas exposed on the high- and low-pressure sides.

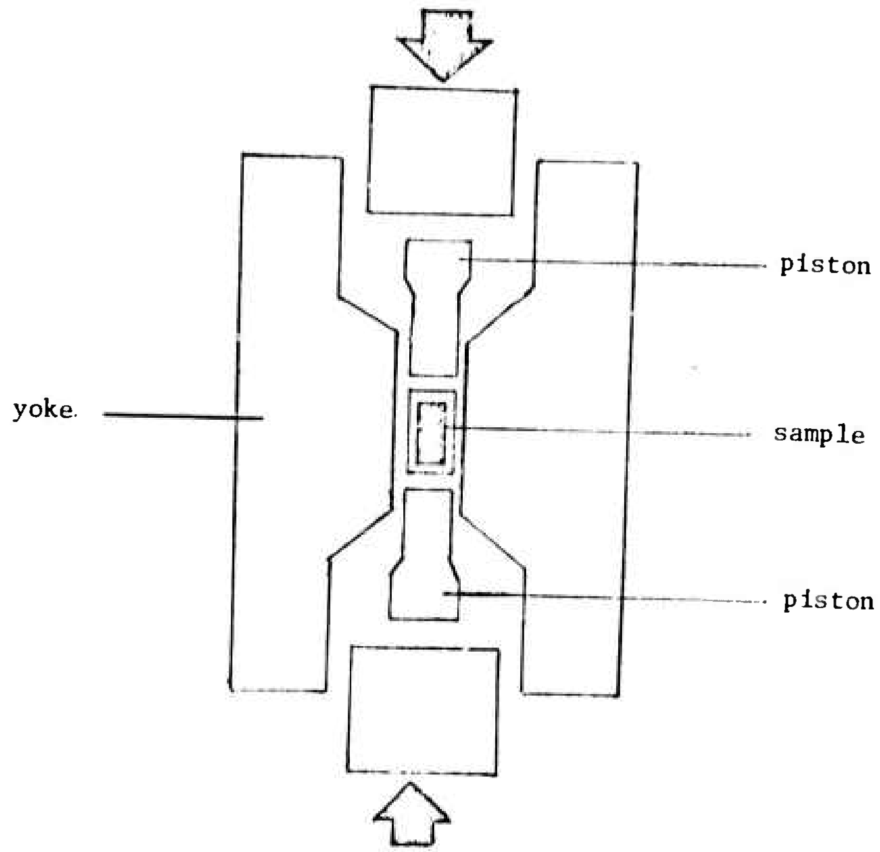

Figure -- Bridgman's two-piston single-axis compression apparatus

An early design contribution (1944) by Soviet investigators was the ingenious "ice bomb" of Lazarev and Kan at the Ukrainian Physico-technical Institute. This device was a considerable departure from rather than merely a modification of Bridgman's apparatus. It provided up to two kilobars, using the increase in the volume of water on freezing. Some control of pressurization by this means was obtained in subsequent developments through the use of ethyl alcohol solutions in place of pure water. A decade later, the ice bomb method was used in the Soviet Union to investigate the superconducting properties of cadmium under a pressure of ~ 1.6 kbar at ultralow temperatures. Analogous methods utilizing fluids that are converted to solids in the course of pressurization followed including the kerosene bomb [25]

developed by Itskevich, permitting work up to 7 kbar and the use of solid helium at up to 10 kbar in Schirber's studies [41].

A further improvement in static press design was the pressure chamber developed by Wittig of West Germany in 1966. The enclosure in which the experimental sample was placed was made in the form of a pressure-retaining ring with upper and lower disks. A subsequent Soviet modification of this structure, namely, a reduction in size and the use of two retaining rings, gave an increase in working pressure to 300 kilobars [10].

The friction of the pistons and sample with the chamber wall in the Bridgman press gave an appreciable loss of pressure within the sample. Brandt and Ginzburg found that a lubricant of graphite on thin cigarette paper reduced the friction by 96 percent [10]. Such remarkable improvements in detailed aspects of the apparatus have been important in increasing experimental capability.

Of course, the development of structural materials has been as significant in reaching high pressure as the geometric design of the apparatus. Some presses use direct mechanical action of levers, pistons, screws, and nuts. In others, a hydraulic medium transmits the force to the sample. Oil, kerosene, ice, solid hydrogen, solid helium, and silver chloride have been investigated as hydraulic substances. The hardest known alloys, such as tungsten carbide alloys, have been used for metal components directly involved in generating pressure. Diamond has been considered for anvils applying the pressure to the sample being studied. In the USSR, Vereshchagin's Institute of High Pressure Physics reported the synthesis in 1972 of carbonado diamond, microcrystalline diamond that was tested up to 2.5×10^6 kg/cm^2 in the form of anvils [47, 49, 50]. The material is approximately twice as hard as natural diamond. This was a successful follow-up of a suggestion made by Bridgman thirty years previously for the improvement of natural diamond, which Bridgman held unsatisfactory for high-pressure applications on account of porosity. The improvement in properties of the fine-grain synthetic diamond may be compared to the earlier development of a hardened microcrystalline glass structure known as pyroceram.

B. SHOCK WAVES

Some recent reports of alternate pressurization methods are of interest. Inspired by the possible transformation of hydrogen to a metal at sufficiently high pressure, researchers have considered shock waves for compression of this element. The pressure at which the transformation may occur has been estimated as greater than that generally accessible with static presses, but readily obtained in a shock. However, problems associated with shock-induced pressure -- destruction of sample and short-lived effect -- by far outstrip problems inherent in static pressure methods. Diagnostic measurements of the parameters of state are extraordinarily difficult in the extremely short times involved. In addition, the shock wave produces marked heating to the order of 10^4 K, strongly limiting the actual compression obtained. By converting the shock wave compression from the usual adiabatic process, as expressed by the Hugoniot equation, into an isentropic mode, the temperature increases caused by entropy contributions from the shock are avoided; and high compression can be achieved.

Three studies were reported by Soviet researchers involving the use of shock waves for isentropic compression, especially of hydrogen [3, 20, 21]. At the Institute of Chemical Physics, the Hugoniot curves were calculated with increasing densities, indicating that, with appropriate mass density increase in the shock compression, isentropic conditions could be achieved [28]. Following this result, a group at the Institute of Optical and Physical Measurements gave a more detailed physical description of an experimental device, similar to that used in the preliminary studies with hydrogen [3]. This was the already familiar metal cylinder apparatus which is compressed by an explosion [27]. A computation for compression of solid hydrogen by two copper plates approaching one another at a velocity of 2 km/sec was reported. For compression to a final pressure of over one megabar, less than 4 percent was contributed by thermal pressure, indicating the effectiveness with which unnecessary heating (isentropic vs. adiabatic compression) is minimized by this method.

C. ELECTRON BEAM

Bogdankevich and Rukhadze of the Lebedev Physics Institute proposed the use of a strong-current relativistic electron beam to produce a high pressure in the small volume of vaporized and ionized material on which the beam impinges [8].

The parameters required to generate the necessary conditions in a 0.5-cm sphere were estimated. The material involved would be a small granule of a readily ionized substance placed in liquid hydrogen and near the surface, for the case of metallizing hydrogen. To get a pressure of one megabar, which corresponds to the electron density of 1.5×10^{23} cm^{-3}, the 5 MeV beam should deliver an energy of 50 kJ in a current of 10 kA. A pulse less than two microseconds, but considerably longer than 3 nanoseconds, would be required by space charge and electron- and ion-velocity limitations.

D. LASER RADIATION

Compression by laser radiation has also been suggested in the context of the metallic hydrogen problem [4]. This is a simpler application derived from consideration of compression of fuel in laser fusion [15]. For fusion, a compression of approximately 10^4 times the solid state density is necessary; this corresponds to a pressure of approximately 1 Tbar (one trillion atmospheres). With respect to the metallic hydrogen problem, a compression of only one order of magnitude is probably sufficient for the megabar pressures. From approximations for a simple piston model, a laser pulse of approximately 2 kJ was estimated to provide 5 Mbar pressures in a layer 0.1 thick [4]. Although in this case adiabatic compression and avoidance of strong shock waves would be desired, the problem has fewer constraints than the implosion of a fusion fuel for which a good pulse characterization, target sphericity, and symmetrical compression are essential.

III. RECENT STUDIES IN HIGH-PRESSURE SUPERCONDUCTIVITY

Soviet and American papers on high-pressure superconductivity published from 1971 to June 1974 are discussed separately in this Section to show the major areas considered important to HPS programs in each country. All of the significant papers that have appeared are indicated, although the survey is not exhaustive.

A. RESEARCH IN THE USSR

1. Rhenium Carbide

A group at Vereshchagin's Institute of High Pressure Physics reported the first preparation of cubic face-centered (NaCl structure) rhenium monocarbide [39]. The material was superconducting at a T_c of 3.4 ± 0.2 K. In previous work, the same group prepared a hexagonal structure at pressures above 60 kbar and temperatures above 800 C which was not superconducting down to 1.6 K. The hexagonal carbide is stable up to 144 kbar.

The cubic phase was prepared by subjecting electrolytic rhenium (99.99%) and spectroscopically pure graphite to 160 to 180 kbar at 100 C for 2 to 5 minutes. For experimental pressure stability, the initially powdered reagents were first mixed and sintered at 90 kbar and 500 C. The absence of metallic rhenium and of graphite from the X-ray powder spectra led to the conclusion that most of the products were pure. The rhenium monocarbide is metastable at atmospheric pressure; heating at 1000 C in vacuum for two hours converted the compound to a solid solution of rhenium and carbon.

The superconductivity of this substance added support to the rule that Group VII transition metals (Tc, Re) give lower T_c in their cubic monocarbides than those of the Group VI metals (Mo, W).

No direct, accurate analysis of the rhenium monocarbide was made, however, and there is the possibility that a nonstoichiometric composition was present in the material. This presumably would cause a reduction of the observed T_c from the one for an accurate composition.

2. Metallic Iodine

Vereshchagin and coworkers confirmed previous work on the metallization of iodine under pressure, while determining the pressure required for the transition (135 to 138 kbar) more accurately [48]. The resistivity was approximately 10^{-4} ohm·cm. Iodine is of interest since it is the nonmetallic element requiring the lowest pressure for conversion to a metal, and Vereshchagin was interested in the possibility that information useful in the problem of transforming hydrogen to a metal might be obtained. The latter question has become one of the major research interests of Soviet high-pressure programs.

3. Zinc and Cadmium Stannous Arsenides

A group at Vereshchagin's institute published further work clarifying the behavior of $ZnSnAs_2$ and $CdSnAs_2$ under pressure [27]. Western scientists had suggested previously that $CdSnAs_2$ was converted into a new cubic phase under pressure. At pressures of 10 to 100 kbar and temperatures up to 500 C, a superconducting material with a T_c of approximately 2 K is produced. By X-ray analysis and study of the analogous compound $ZnSnAs_2$, the Soviet scientists showed that a chemical decomposition occurs

$$3MSnAs_2 \rightarrow 3SnAs + M_3As_2 + As$$

in which M is cadmium or zinc. The product tin arsenide, SnAs, accounts for the superconductivity with the observed transition temperature. Thus, a decomposition of the initial compounds on heating under pressure is involved, rather than a phase transition.

4. Potassium and Rubidium

Transition of potassium and rubidium to superconductivity at 150 kbar and 100 kbar, respectively, was estimated theoretically by investigators at the All-Union Scientific Research Institute for Optophysical Measurements [17]. The conductivity was described with wave functions and a Wigner-Seitz approximation for the band structure.

With initial increases in pressure, there is a rearrangement of s- and d-bands, leading to greater localization of electrons accompanied by an increase in resistivity. The resistivity is a maximum with respect to compression when the d-band fills up, which occurs at a compression of 2.5-fold on potassium and 2-fold on rubidium. The superconductivity was derived from the same type of pressure effect on the conduction electrons using the electron plasma frequency and estimated coupling for the BCS theory.

5. Bismuth, Barium, and Lead

Previous measurements on these elements were extended to the pressure range of 100-200 kbar by Itskevich and colleagues [23]. Several additional high pressures were used to give an improved coefficient of variation in T_c for the much-studied bismuth (VI), $-(2.3 \pm 0.5) \times 10^{-2}$ K/kbar.

Barium appears to undergo a transition under approximately 150 kbar. The T_c is 4.85 K at 164 kbar; up to 200 kbar the variation of Ba (IV) is $(1.3 \pm 0.5) \times 10^{-2}$ K/kbar. Previous measurements by Wittig and Matthias were approximately 0.4 K higher in T_c, a discrepancy attributed by these authors to experimental errors in temperature and pressure.

For Pb (I) the variation in T_c was $-(1.1 \pm 0.5) \times 10^{-2}$ K/kbar up to 160 kbar in agreement with previous results of Wittig. For Pb (II) above 160 kbar, the variation was approximately $-(2.2 \pm 0.5) \times 10^{-2}$ K/kbar, based on only a few experimental points.

6. Tantalum and Niobium

Brandt and colleagues at the Moscow State University extended previous studies of tantalum and niobium to greater pressures (to 250 kbar) [5]. Increasing pressures from 0 to 20 kbar on tantalum give a regular decrease in T_c, with dT_c/dp of $-(2.6 \pm 0.1) \times 10^{-3}$ K/kbar. At greater pressures -- 100 kbar and above -- the parameter decreases almost to zero. The transition temperature of niobium drops sharply from atmospheric pressure to 25 kbar. Although the original bulk material displayed the transition to superconductivity at 9.2 K at atmospheric, the observed decrease in this range appeared to be from approximately

9.5 K to slightly less than 9.2 K. The pressure measurements reported were too inaccurate to permit evaluation of dT_c/dp in this pressure range. With further increase in pressure, T_c decreases to a minimum, and then from approximately 50 kbar, increases linearly with a slope $dT_c/dp = 2.6 \pm 0.2 \times 10^{-3}$ K/kbar.

A contrast between tantalum and niobium was observed: T_c of tantalum is insensitive to impurities, dissolved gases, and stresses; T_c of niobium is markedly affected by these. Sensitivity to plastic deformation was given as the cause of the different T_c dependences with pressure in niobium. There is insufficient information concerning the effect of pressure on other properties, such as volume or energy spectra, to account for the variation in T_c.

7. Tellurium

The behavior of tellurium under pressure is quite different from that of tantalum and niobium, discussed above, in work reported from the same group at Moscow State University [6]. There are four modifications, and three of these, Te (II), (III), and (IV), appear to be different superconducting crystal forms. Bridgman reported three decades earlier on the transition of Te (I) to Te (II) at 39 to 40 kbar and Te (II) to Te (III) at 69 kbar. The superconductivity was examined up to 260 kbar by the investigators associated with Brandt. The value of dT_c/dp observed for the various modifications in the respective ranges of pressure were: Te (II) -- 40 to 70 kbar, $7.7 \pm 1 \times 10^{-2}$ K/kbar; Te (III) -- 70 to 80 kbar, $-(0.3 \pm 0.1) \times 10^{-2}$ K/kbar; and Te (IV) -- 80 to 100 kbar, $-(4.2 \pm 1) \times 10^{-2}$ K/kbar. Earlier work by Il'ina and Itskevich was in general agreement with these results [22].

The pressure variation of T_c in Te (II) is the largest known. At 110 kbar, there was a further change in dT_c/dp, reported by the authors as measured at $1.0 \pm 0.5 \times 10^{-2}$ K/kbar. This may also be interpreted, in the absence of a more complete investigation, as a gradual modification to the higher pressure state to 180 to 260 kbar, where T_c remains almost invariant. The experimental data from 100 to 160 kbar may be interpreted either as a straight line, or equally well, as a smooth curve. The appearance of new crystal forms in the

transitions at up to 100 kbar are supported by Mössbauer spectra, but such data are lacking for the higher pressures.

8. Vanadium

A comparison of Soviet with other studies on a thoroughly investigated substance such as vanadium provides a good basis for evaluating the level of Soviet research in this field. Table 1 presents previous measurements of dT_c/dp and the most recent determination from Brandt's group at Moscow State University [11].

The Soviet work extended the studies over a considerably greater range and provided a value in reasonable agreement and of equal precision as the measurement from a Western laboratory made at almost the same time. Soviet measurements were carried up to 250 kbar. Above 150 kbar dT_c/dp decreased from linearity. The results were interpreted in terms of McMillan's strong-coupling expression for superconductivity. The sensitivity of T_c to plastic deformation at low pressures and its high rate of change in general may explain the disagreement between different pressurization methods.

Table 1

VARIATION OF T_c WITH PRESSURE FOR VANADIUM

dT_c/dp, K/kbar	Pressure Range, kbar	Investigators
$1.1 \pm 0.3 \times 10^{-2}$	0-10	W. E. Gardner, T. F. Smith, 1966
$1.76 \pm 0.15 \times 10^{-2}$	0-45	D. Köhnlein, 1968
$0.62 \pm 0.03 \times 10^{-2}$	0-24	T. F. Smith, 1972
$0.70 \pm 0.03 \times 10^{-2}$	0-150	N. B. Brandt, O. A. Zarubina, 1973

9. Yttrium

Brandt, Berman, and Kurkin of Moscow State University studied yttrium up to 160 kbar and concluded that several modifications are involved, contrary to the previous results of Wittig [9]. Wittig

suggested that the pressure effects are continuous and arise from the regular increase in electron density on compression [51]. The Soviet work, on the contrary, was interpreted as showing that above 110 kbar (the pressure at which both laboratories report the appearance of superconductivity) Y (II) occurs with dT_c/dp of $-(3.2 \pm 1) \times 10^{-2}$ K/kbar. At approximately 125 kbar, the pressure effect changes markedly to $(3.5 \pm 1) \times 10^{-2}$ K/kbar, a value in accordance with the previous report by Wittig, but designated Y (III). A further transition was claimed at 140 kbar to Y (IV), based on a sudden change in critical field, although the variation in T_c remains almost the same.

10. Lanthanum

Zarubina of Moscow State University extended measurement of T_c for lanthanum up to 250 kbar [52]. As in previous studies, T_c increased markedly with pressure in the lower range from below 5 K at atmospheric to approximately 11 K at 70 kbar. Above this pressure, the change in T_c with pressure decreases markedly, and T_c appears to be pressure-independent from 100 to 250 kbar.

The presence of both α (close-packed hexagonal) and β (face-centered cubic) phases is recognized at room temperature, with conversion entirely to β-phase at 23 kbar at this temperature. The T_c's of the two structures at p = 0 are 4.88 K and 6.04 K, respectively.

The superconductivity of lanthanum indicated in these observations has not been fully explained. It was suggested earlier, based on the effect of the 4f band slightly above the Fermi surface, that superconductivity was caused either by increased interaction of conduction electrons with the 4f band, or by magnetic interaction from only partial filling of the band. Increasing the pressure, however, should decrease the energy gap between this band and the Fermi level, and thus, the change in T_c would be the opposite of what was observed.

Another model proposes the isolation of the 4f-level from the superconducting level. With increasing pressure, the 4f-states empty until none is occupied, and the T_c increases as the 4f-level contributions to conductivity cease. Zarubina objected that this process does not explain the nearly linear increase in T_c from 50 to 140 kbar reported in earlier work. Instead, she suggested the possibility of

a polymorphic transition at 70 to 100 kbar, which would be in accord with the irregularity in the variation of lanthanum resistance with pressure at 70 kbar and room temperature.

11. Titanium-Niobium Alloys

Complex phase equilibria in titanium-niobium alloys exhibiting superconductivity were investigated jointly by groups at the Institute of Chemical Physics and the Moscow Institute of Steel and Alloys [2]. Compression of the alloy containing 10 at% of niobium at 120 kbar produces ω-phase, which is metastable when the pressure is released. Lower pressures applied to the alloys of 10 percent niobium and compression up to the maximum investigated (120 kbar) of 20 percent alloys (or above) give only partial conversion to the ω-phase, which reduces the T_c of the alloy. The ω-phase may be produced under appropriate conditions by heat treatment, and the structure and lattice dimensions appear to be the same, except in this case the T_c of the alloy increases.

12. Niobium-Aluminum-Germanium Alloys

A study of the effect of pressure on T_c was made for these ternary alloys with the A15 structure, which exhibited the highest accessible superconducting temperatures -- up to 20.29 K [16]. The compositions giving stable A15 structure were investigated up to 38 kbar. In Nb_3Al, a first order phase transition occurs at 17 kbar in which there is a 1 percent decrease in volume, and T_c increases from 17.11 K to 17.5 K. In all the other alloys, T_c varies linearly with pressure. The alloys in the phase diagram near the phase equilibrium or on the boundary of the single-phase region are most sensitive to deformation. As germanium increasingly replaces aluminum in its compound with niobium (forming the ternary alloy with increasing amounts of germanium), dT_c/dp changes sign twice. This indicates singularities in the change of state density at the Fermi surface with composition.

13. Bismuth-Indium Alloys

A study of bismuth-indium alloys under pressure showed the formation of the X-phase and associated superconductivity, similar to the bismuth-tin system [30]. Dilatometric measurement was used to observe

the volumetric change associated with phase transitions. The change in transition temperature for superconductivity with pressure (dT_c/dp) of the alloy containing 74 at% bismuth measured in this way was $-(2 \text{ to } 3) \times 10^{-2}$ K/kbar. Pressures up to 35 kbar were used in this work. T_c generally fell between 7 and 8 K in systems with above 53 at% bismuth.

14. Niobium Diselenide

The change in T_c of $NbSe_2$ with pressure is 4×10^{-2} K/kbar up to 60 kbar [24]. A new modification is produced above 60 kbar, with T_c of 8.9 K at 64 kbar (vs. 6.4 K for the initial form at 0 pressure). The T_c variation with the decrease in interplanar distance in the crystal indicates that superconductivity involves an interaction between niobium planes. The T_c in the compound intercalated with pyridine shows a specific interaction greater than the distance between planes alone can explain.

15. Theoretical Studies

Khomskiy of the Lebedev Institute undertook the difficult task of correlating the behavior of the transition metal superconductors under pressure [26]. The variation of the logarithms of T_c with the compression (volume) was examined in terms of the parameters of Hopfield's theory and McMillan's strong coupling. The values of $d\ln T_c/d\ln v$ show considerable dispersion, even changing in sign. Table 2 presents the parameters that were evaluated: γ_G is the Gruneisen coefficient, λ the electron-phonon interaction constant, η a measure of the band width $\exp(-\chi r)$ using 2.7 $\mathring{A}^{-1}$ for χ with the atomic radius r, and ζ the logarithmic variation of this zone parameter with compression $-d\ln\eta/d\ln v$. Reasonable agreement is reported by the author in the function

$$\frac{d\ln T_c}{d\ln v} = -\gamma_G + \frac{\lambda(1+\mu)}{(\lambda-\mu)^2}(2\gamma_G - \zeta)$$

with the parameters given, when $\mu = 0.13$.

Table 2

TRANSITION METAL SUPERCONDUCTIVITY PARAMETERS

	$\frac{d\ln T_c}{d\ln v}$	γ_G	λ	ζ	η
Ti	-15	1.33	0.38	4.66	1.47
V	-3.4	1.55	0.60	3.70	2.53
Zr	-21.6	0.82	0.41	5.15	1.53
Nb	0	1.74	0.82	2.31	3.74
Mo	4.0	1.65	0.41	2.34	3.85
Tc	4.6	2.75	0.71	3.75	
Ru	0	3.25	0.38	6.02	
Ta	1.2	1.82	0.65	2.53	3.44
Re	5.1	2.66	0.46	3.69	4.33
Os	11.8	2.02	0.30	1.81	
Ir	18.5	2.40	0.34	1.54	
V_3Si	-3.20	1.55	0.82	3.98	

The relationship of the electron states involved in superconductivity with other physical properties of a substance, such as the specific heat and elastic modulus, leads to the possibility of studying the effect of pressure on superconductivity indirectly, through its effect on the other parameters. Thermodynamic relationships among these parameters and T_c have been a major study. Palistrant [36, 37] has examined the effect of shape of the Fermi surface on the variation of superconductivity and specific heat capacity with pressure. In a two-band superconductor, he predicted two extrema in dT_c/dp [37]. In the most extensive recent paper on thermodynamic properties in the period covered by this review [36], Palistrant investigated the effect of pressure on T_c, the order parameter, critical field, and heat capacity in doped superconductors with specified density of electron states (Van Hove singularities). The variation of these properties was obtained in terms of the Fermi energy, or equivalent frequency.

B. RESEARCH IN THE UNITED STATES

1. V_3Si and V_3Ge

Investigation of theoretical thermodynamic relationships among superconductor properties has also received attention in recent U.S. work. Published studies have dealt with V_3Si, a compound of major interest in strong coupling theory. Part I of this Review,* which treated high-temperature superconductivity, discussed the prediction of maximum T_c for V_3Si of 40 K and the possible sources of failure of this prediction, such as lattice instability and limitation of the coupling interaction to less than 2, the maximum theoretical value.

Sham and Smith at the University of California, San Diego, investigated the relationship of T_c with elastic properties in V_3Si and V_3Ge [43]. They found, as did previous workers, that a large, quadratic dependence of T_c on strain is to be expected from a thermodynamic analysis. The experimental data from acoustic measurement of the bulk elastic modulus exhibits a large discrepancy from the theory. A much lower variation of T_c with pressure is indicated. The authors pointed out that second order terms can be significant, but even when they were taken into account, a very large discrepancy remained. They could only suggest that differences between relatively small terms in the modulus may have a large effect, necessitating very accurate measurements near T_c; but no conclusive explanation of the discrepancy was provided by their study.

The change in a lattice parameter of V_3Si with pressure at room temperature was not according to the normal cubic variation [7]. Above 15 kbar there appears to be a distortion that could be a transformation from the normal A15 cubic structure to tetragonal. The transformation is reversible; on reduction of the pressure to atmospheric, the A15 structure reappears.

Carcia and Barsch at Pennsylvania State University compared dT_c/dp for V_3Si calculated from modulus measurements with the value calculated

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*Y. Ksander and S. Singer, *Advanced Concepts of Superconductivity: A Comparative Review of Soviet and American Research. Part I. High-Temperature Superconductivity*, The Rand Corporation, R-1401-ARPA, January 1974, pp. 14-16.

using an anisotropic Debye approximation [12]. A low temperature structural change can occur in V_3Si. The calculated dT_c/dp for non-transformed material was 2.5 times the experimentally derived value. The calculated dT_c/dp of transformed V_3Si was approximately one-sixth the same experimental value; but no experimental measurement was available for transformed V_3Si.

These studies show that the indirect determination of dT_c/dp by measurement of other properties is open to question even when the thermodynamic relationships seem quite clear.

2. Pu_2C_3 Structures

A number of thorium sesquicarbides containing varying amounts of other metals have been prepared under pressures of 15 to 40 kbar. The material with the highest T_c resulting from high-pressure synthesis was found in this work. The yttrium-thorium sesquicarbide $(Y_{0.7}Th_{0.3})C_{1.55}$ formed at 15 to 25 kbar exhibits a T_c of 17.0 K (at 1 atmosphere) [29]. The structure produced at high pressure is the body-centered cubic commonly referred to as the plutonium sesquicarbide structure (bcc Pu_2C_3).

3. $AuGa_2$ and Its Alloys

Experimental work in the United States during the period covered in this review (that is, the period following the publication of the last review of this field by Brandt and Ginzburg [10]), included study of the $AuGa_2$ compound and its alloys. A change in T_c of 0.8 K from approximately 1.2 to 2.0 K was observed by Schirber in $AuGa_2$ under 6 kbar pressure [42]. This provides strong evidence for a pressure-induced electronic transition in the material at liquid helium temperatures and approximately 6 kbar pressure. A high density of states is involved, with a change of perhaps 10 percent in the state density with the transition. An electronic transition appeared likely in earlier work on Tl, InCd, and Re; but the small changes in T_c with pressure in those substances made a positive conclusion more difficult. There were strong indications of the transition in $AuGa_2$ in previous studies of doping and of the band structure. Alloying of the compound

with palladium addition was ascribed to lowering of the Fermi surface and electron scattering, which broadens the otherwise very high density of states in the initial $AuGa_2$ [45]. Most of the change in T_c was credited to the effect of state density.

4. Nb_3Sn

Chu and Testardi observed a lattice transformation in Nb_3Sn from cubic to tetragonal up to 18 kbar [13]. The temperature of transformation (T_t) increased with pressure, linearly at high pressure with $dT_t/dp = 2.8 \pm 0.1 \times 10^{-1}$ K/kbar. Over the same range the superconducting transition temperature decreased with $dT_c/dp = -(1.40 \pm 0.05) \times 10^{-2}$ K/kbar.

5. In and Cd-Pb Alloys

T. F. Smith of University of California at San Diego examined dT_c/dp of indium and its dilute cadmium and lead alloys up to 24 kbar [44]. The variation in T_c was interpreted in terms of the shape of the Fermi surface of indium. The decrease of T_c as pressure increased was not linear; four transitions were evident. One occurred on alloying with 0.5 at% of cadmium or less; a pressure of 8 kbar prevented this transition. The second arose with 1.5 at% cadmium or more, and was prevented by the application of more than 5 kbar pressure. The third transition could be produced either by applying 6 kbar to indium alone or by alloying with 2 at% of lead. A transition also occurred with 7 at% of lead, regardless of the pressure. Other indications of these changes in the Fermi surface had been noted previously in the thermoelectric power, critical magnetic field, electronic specific heat, and magnetic susceptibility.

6. Intercalated Structures

The pressure dependence of T_c for a layered, intercalated superconductor, of interest as an example of anisotropic electronic systems, has been investigated [46]. $TaS_{2-x}Se_x$ gave a maximum T_c of 4.1 K with $x = 0.4$. Pressure up to 25 kbar increased the T_c. Intercalation reduced the variation of T_c with composition; pressure also increased the T_c of intercalates, but not as greatly as in the original material.

IV. ASSESSMENT OF SOVIET AND U.S. RESEARCH IN HIGH PRESSURE SUPERCONDUCTIVITY

This Section discusses the current status of Soviet research in high-pressure research and compares it with the U.S. effort. Table 3 lists Soviet and Table 4 U.S. institutions and scientists affiliated with them engaged in investigations of the effects of high pressure on the superconducting properties of materials. At least half a dozen major institutions in the Soviet Union are involved in research on superconductivity under high pressures. Of these, the Institute of High Pressure Physics is most prestigious and has the best program in this area; its research activity is highlighted in this Section as an example of the Soviet technological capability in a potentially high-yield area of research.

A. THE INSTITUTE OF HIGH PRESSURE PHYSICS, USSR ACADEMY OF SCIENCES

The Institute of High Pressure Physics, just outside Moscow, is without peer in facilities for work in this field. Only a handful of institutes can match it for high quality of technical equipment, but not for quantity and scale. This is due in part to the requirements of the work being done there. Its apparatus is comparable to the best in Western laboratories, excepting the high-pressure presses, which surpass all others. Furthermore, the Soviets' advantage may be expected to increase with completion of a new 50-kiloton press now under construction.

The Institute of High Pressure Physics has a staff of approximately 500, of whom 100 are professionals. Its standing in the Soviet hierarchy may be gauged by an anecdote related with pride by L. F. Vereshchagin, its highly respected director. At the end of a tour of the institute by Soviet government officials in 1972, the Minister of Finance asked if the institute could use an additional ten million rubles in its annual budget; Vereshchagin replied that his funds were already adequate.

Table 3

SOVIET RESEARCH IN HIGH-PRESSURE SUPERCONDUCTIVITY

Institutions	Scientists
Institute of High Pressure Physics	Vereshchagin Arkhipov Itskevich Popova, Fomicheva, Khvostanstev, Boyko, Stepanov, Kabalkina Yakovlev, Bibayev, Vinogradov Varfolomeyeva, Slesarev, Shterenberg Semerchan, Kuzin, Sadkov
Moscow State University	Brandt, Ginzburg Zarubina, Berman Kuz'min, Opalenko, Slobodchikov
Institute of Chemical Physics	Kompaneyets Romanova, Yampol'skiy
Moscow Institute of Steel and Alloys	Afonikova Degtyareva, Litvin, Rabin'kin, Skakov
All-Union Scientific Research Institute for Opticophysical Measurements	Gandel'man Itskovich, Kondratenko, Perstnev, Finkel'berg Voropinov, Podval'nyy Al'tshuler Dynin, Svidinskiy
Lebedev Physics Institute	Khomskiy
Baykov Institute of Metallurgy	Shinyayev, Fedorov, Gorshkova, Chernov
Landau Institute of Theoretical Physics	Abrikosov Anisimov
Institute of Applied Physics, Academy of Sciences, Moldavian SSR	Palistrant, Kolpagiu
Uzhgorod State University	Laukhin, Mamushchenko, Rabin'kin

Table 4

U.S. RESEARCH IN HIGH-PRESSURE SUPERCONDUCTIVITY

Institutions	Scientists
University of California, San Diego	Smith (now at CSIRO, Australia) Sham Shelton Schwall
Bell Telephone Laboratories	Testardi McWhan
Sandia Laboratory	Schirber
Los Alamos Scientific Laboratories	Krupka, Giorgi Krikorian, Szklarz
Cleveland State University	Chu
Pennsylvania State University	Carcia Barsch

Under Vereshchagin's direction, the Institute of High Pressure Physics developed and now produces synthetic industrial diamonds, fulfilling a national requirement projected several years ago by Soviet planners. The purview of the organization goes beyond the manufacture of the raw synthetic material. The institute produces precision-finished industrial items of diamond: nuts, bolts, screws, cylinders, and bearings. The synthetic material is much harder than natural diamond, typically twice as hard, making available long-lasting machine tools. One example is drills which seldom have to be replaced. The technological section of the institute has developed a small, high-speed motor (12,000 rpm) running on diamond bearings, intended for control applications and airplanes.

Precision dimensions, accurate threads, and unusual shapes are produced by machining diamond-grade graphite to the desired design and then converting the material to diamond in the production press. The effect of the conversion on the dimensions is readily taken into account. Synthetic diamonds up to 25 carats may now be prepared on the production press which has a one-meter diameter ram and a capacity of 10,000 tons force. Single diamonds up to 100 carats will be

obtainable in a future apparatus. Vereshchagin estimated the cost of the industrial diamonds at $10 to $15 per carat. His institute is also investigating the preparation of gem-quality stones, which he estimated would cost approximately twice as much. The synthetic gems made in the United States by General Electric and Westinghouse are 100 times costlier (approximately $3,000 per carat). However, the real costs of U.S. and Soviet synthetic gems may be closer than these estimates indicate, as Vereshchagin no doubt tends to minimize his cost while the U.S. manufacturers appear to overestimate theirs.

Solid-state electronic devices based on diamond will be an area of future interest at the Institute of High Pressure Physics. In terms of such desired characteristics as stability at high temperature, synthetic diamond is expected to be an improvement over existing materials -- silicon being the most extensively used matrix at present. Vereshchagin has prepared a p-type semiconductor by doping diamond, but no junctions have been obtained as yet. This field has been considered in the United States, in part by study of natural, colored diamonds. The color is in some cases due to natural impurities which play the role of a dopant and confer potentially valuable electronic properties.

B. SOVIET EXPANSION OF HIGH PRESSURE FACILITIES

A major increase in the high-pressure research capability of Vereshchagin's institute is under way with the construction of a 50,000-ton press at an estimated cost of $14 million [47]. The press will occupy its own building, a structure over 10 stories high, which is nearing completion. The primary function of the new press is said to be the investigation of the properties of hydrogen under superhigh pressures.

Rand is presently reviewing research concerning the conversion of hydrogen into the superconducting state. Suffice it to say here that hydrogen has been the subject of considerable theoretical study by the Soviets and of experimental work on compression by detonation in both the USSR and the United States. The conversion of molecular hydrogen into the metallic state has been predicted at pressures varying from

0.25 to 20 megabars by several theoreticians since 1935. B. Matthias recently stated that on the basis of cesium superconductivity and the properties of hydrogen phases, the T_c of metallic hydrogen should be 15 to 20 K [33], in contrast to theoretical predictions that have indicated the possibility of a transition temperature as high as 200 K. The appearance of superconductivity in the metallic phase has been proposed by a number of investigators. Recent experimental data from shock-wave compression studies at Lawrence Livermore Laboratory [20] and at an unidentified Soviet laboratory [19] have shown a sudden change in density at 2 to 2.8 megabars, possibly indicating condensation into the metallic phase.

C. COMPARISON OF SOVIET AND U.S. RESEARCH

Tables 3 and 4 above provide an indication of relative Soviet and U.S. efforts in the area of high-pressure effects on superconductivity (HPS). In the period from 1971 to June 1974, Soviet investigators published two to three times as many papers as U.S. scientists, indicating that the Soviet activity in this field is at a much higher level. The Soviets have at least 150 full-time professionals working in this area, while the United States supports less than one-tenth of that number.

The difference is much more pronounced than in the research on novel mechanisms for attaining high-temperature superconductivity (HTS), where a systematic and growing Soviet program over the past decade (1964-1973) was nearly matched by a more recent upsurge of interest and activity in the United States. In HPS studies, the trend in the United States appears to be almost the direct opposite, namely, a steady decrease in research activity that will make the gap between the two programs even more evident. In fact, T. F. Smith, who in the past few years has published the largest number of research papers in this field at the Institute for Pure and Applied Physical Sciences of the University of California at San Diego, recently left the United States for Australia.

On the other hand, there are counterindications that the contrast between the two countries is not quite as great as Tables 3 and 4 tend to depict. First, the American scientists shown are only those who have actually published in the period covered by this Report, whereas the Soviet list includes several authors, such as Abrikosov, who are not working continuously in the field. Second, there are a few high-pressure laboratories of some repute in the United States, such as the University of Illinois group, which are not indicated at all because thus far their studies have dealt with materials properties other than superconductivity. Presumably their work could be extended to this field should the occasion demand, since it is the pressure capability which is the most difficult to provide. Third, industrial laboratories in the United States also possess an appreciable technological high-pressure capability, although their work on superconductivity has been limited in the last few years, to judge from publications in the literature.

The contrasts in the Soviet and American programs are based on the different approach to research in this field in the two countries. The Soviet high-pressure studies appear to be directed more as materials programs, including the preparation of new superconducting substances. The current objective of the more theoretical U.S. studies is a thorough understanding of the basic mechanisms of high-pressure effects on superconductivity, and specifically, the shape of the Fermi surface.

The traditionally accepted images of the theory-oriented Soviets and innovation-minded Americans appear to be transposed in this area of endeavor. The Soviet research style -- not generally conducive to rapid exploitation of its own experimental and theoretical results -- is clearly reversed in the case of high-pressure studies. The change is evidently due to the forceful influence of the major figures in this field -- Vereshchagin, Brandt, and Ginzburg.

The relatively small current U.S. effort in the direct study of superconductivity under high pressure may be rationalized in view of appreciable work in progress on other properties of materials at high pressures and a low estimate of the probability that a dramatically improved superconductor will be found by this means. On the other

hand, the discovery of the yttrium-thorium sesquicarbide with a T_c of 17 K by synthesis under pressure may indicate some promise in the method.

Thermodynamic relationships can provide considerable information regarding superconductivity from the observations of other parameters that are more readily studied, such as volume and specific heat. However, the conclusions from such indirect methods may be open to question, and it is conceivable that the greatest doubt will exist in the case of substances with greatest value as superconductors. On the other hand, direct investigation of superconductivity at high pressure seems the most reliable approach, considering the present level of knowledge of relationships involving parameters other than pressure.

Although difficult, it is essential to evaluate properly the significance of the gap between the levels of effort in the USSR and in the United States. In terms of pure knowledge, the situation is far from alarming: U.S. scientists are well informed and their understanding of the basic problems is on a par with that of the Soviet scientists whose papers are read as they become available.

On the other hand, the larger Soviet experimental capability, both in terms of pressure apparatus and in attainable pressure magnitudes in their studies, could be a cause for concern here. We estimate that several years of intensive effort would be required to construct a facility of equal scale and capability in the United States, assuming that the fabrication of large-scale metal components for a press were given top priority. In the meantime, progress toward the development of new materials and new superconductors that may be formed under heretofore unavailable pressures -- the principal thrust of the Soviet program -- is appreciably handicapped in the absence of such a facility in the United States.

Another major Soviet goal is the discovery of superconductors with greatly increased operating temperatures. The high-pressure work provides an additional avenue toward achieving this goal. The Soviet evaluation of the importance of high-temperature superconductors is based on the enormous impact such materials would have on technology, both civilian and military.

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UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

14

1. REPORT NUMBER: R-1579-ARPA

2. GOVT ACCESSION NO.:

3. RECIPIENT'S CATALOG NUMBER:

4. TITLE (and Subtitle): Advanced Concepts of Superconductivity: A Comparative Review of Soviet and American Research. Part II. High Pressure Superconductivity.

6

5. TYPE OF REPORT & PERIOD COVERED: 9 Interim rept.

6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): 10 Yuri Ksander ~~and~~ Stanley Singer

8. CONTRACT OR GRANT NUMBER(s): 15 DAHC15-73-C-0181, ARPA Order-189[redacted]

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
The Rand Corporation
1700 Main Street
Santa Monica, Ca. 90406

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 12 44p.

11. CONTROLLING OFFICE NAME AND ADDRESS:
Defense Advanced Research Projects Agency
Department of Defense
Arlington, Va. 22209

11

12. REPORT DATE: January 1976

13. NUMBER OF PAGES: 44

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):

15. SECURITY CLASS. (of this report): UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report):

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report):

No restrictions

18. SUPPLEMENTARY NOTES:

19. KEY WORDS (Continue on reverse side if necessary and identify by block number):
Superconductivity
Materials
Soviet Union
High Pressure Physics

20. ABSTRACT (Continue on reverse side if necessary and identify by block number):

see reverse side

over

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

The second of three reports on superconductivity, this examines laboratory techniques for obtaining high pressures and their effects on the superconducting properties of materials. (The first, R-1401-ARPA, treated high-temperature superconductivity; the third will discuss high-field superconductivity.) An assessment of U.S. and Soviet research in high-pressure superconductivity (HPS) based on a comprehensive coverage of open-source literature from 1971 through June 1974. Megabar pressure capability is at hand, thanks to development of very hard structural materials. Experimental data are copious, although the pressure range is limited and volume parameters are almost lacking. Soviet HPS research appears to be materials-oriented, American more academic. Hydrogen metallization under superhigh pressure is of major interest in the Soviet new materials program. HPS research has placed the USSR in a position of major strength in this field. ~~33~~ 9 pp. Ref. 2 (Author)